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**SYNTHESIS OF ENERGETIC MATERIALS
ANNUAL PROGRESS REPORT FOR THE
OFFICE OF NAVAL RESEARCH**

WORK REQUEST N0001488WX24105

**M. CHAYKOVSKY
W. M. KOPPES**

MARCH 1988

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**RESEARCH AND TECHNOLOGY DEPARTMENT
NAVAL SURFACE WARFARE CENTER**

DAHLGREN, VA 22448 - SILVER SPRING, MD 20903-5000

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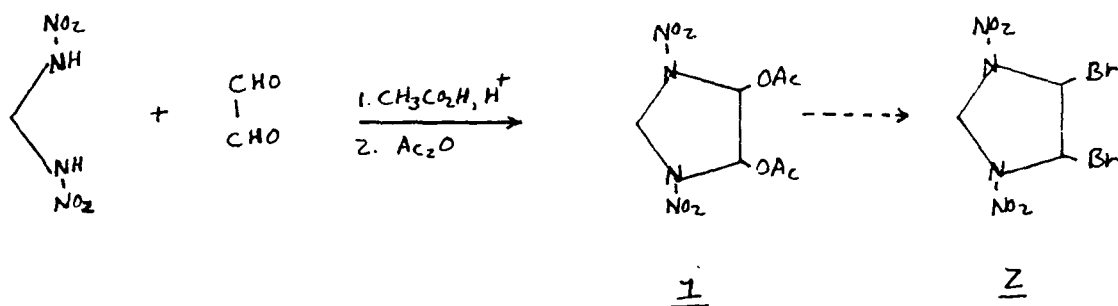
INTRODUCTION

The work described in this report was carried out during 1987 under the sponsorship of the Office of Naval Research, Code 1132P (Dr. R. S. Miller). The principal objective of the work is the synthesis of polycyclic and adamantoid (caged) nitramines with high crystal density and energy-density greater than that of HMX.

SYNTHESIS OF POTENTIALLY DENSE NITRAMINES

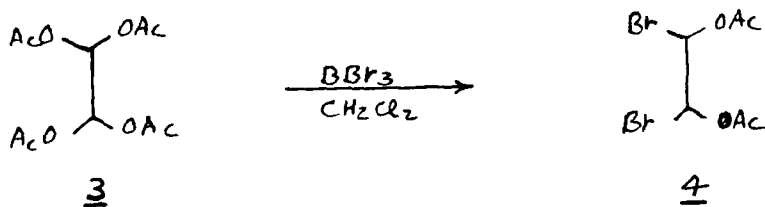
(a) Tetraazabicyclooctanes (Bicyclo-HMX).

During this period, work was continued on the chemistry of cyclic nitramines with the goal of synthesizing bicyclo-HMX and derivatives. In our last annual report¹, we described the synthesis of the diacetoxy-dinitroimidazolidine (1), an intermediate for potential conversion into the dibromide (2), a precursor for the synthesis of bicyclo-HMX.

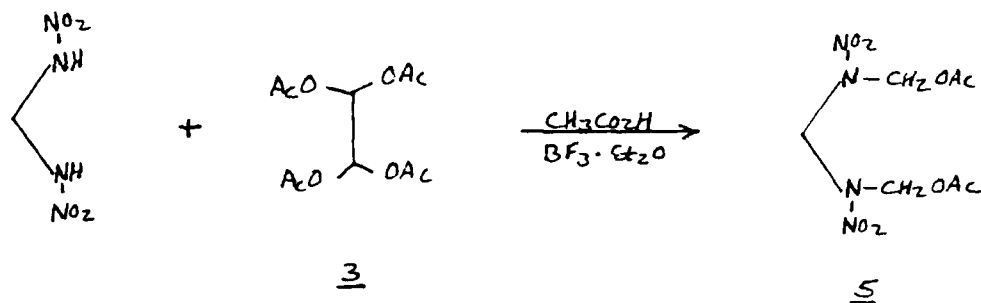


The substituted imidazolidine (1) was prepared by the condensation of methylenedinitramine (MEDINA) with glyoxal in the presence of acetic anhydride. This synthesis, however, was very tedious and proceeded in only about 5% yield. An alternate pathway to 1 was needed in order to obtain sufficient material for further experimentation.

Toward this goal, the known tetraacetoxyethane (3) was prepared by reaction of the trimeric dihydrate of glyoxal with acetic anhydride. This was converted into the diacetoxydibromoethane (4) by ester cleavage with boron tribromide.



Both 3 and 4 were considered as reagents capable of condensing with MEDINA to give 1, under appropriate conditions. In the actual event, MEDINA reacted with 3 in acetic acid, under boron trifluoride catalysis, to give none of the imidazolidine (1), but only a low yield of the MEDINA derivative (5), via an obscure reaction pathway. Under different conditions, the triethylammonium salt of MEDINA reacted with the dibromide (4) to give an intractable resin.

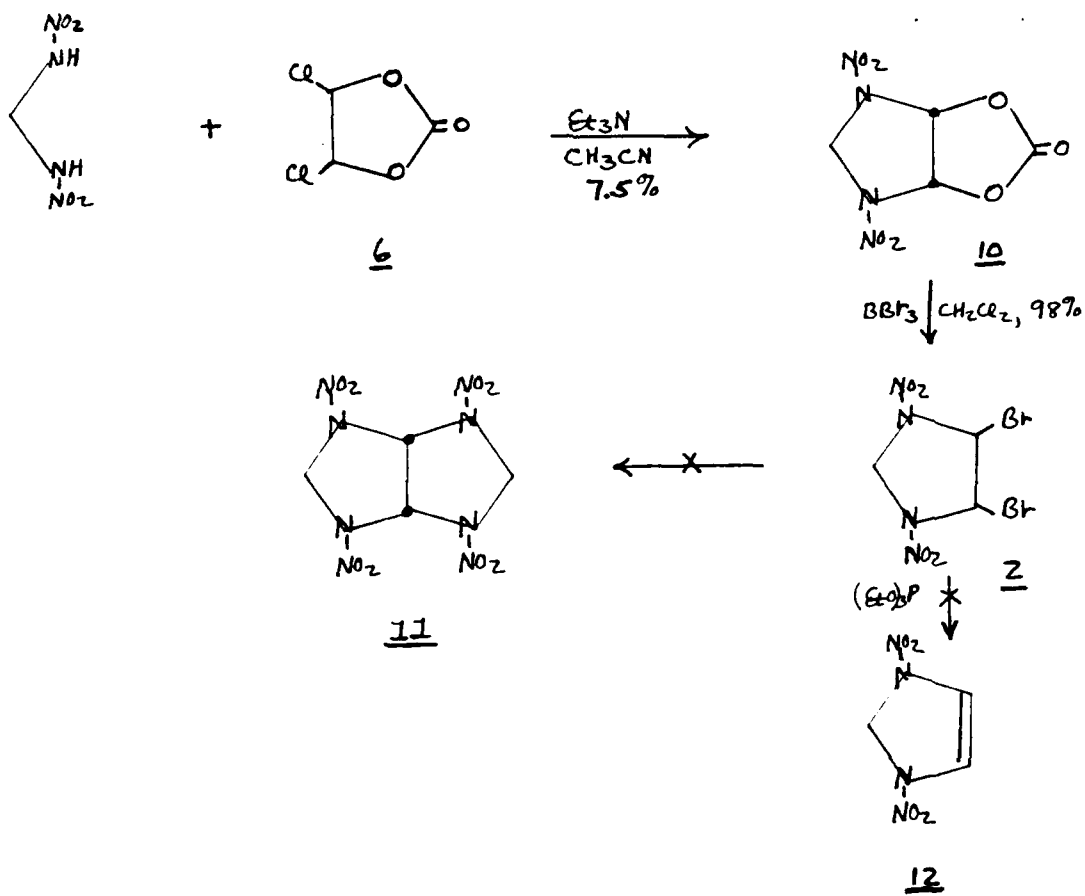
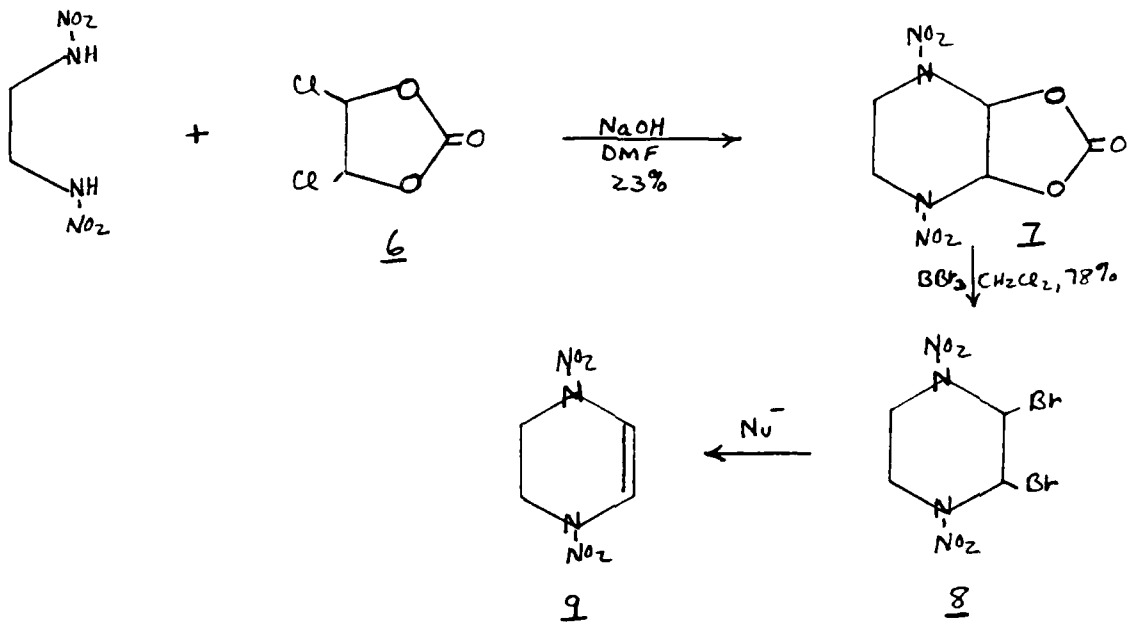


Another reagent which had potential use for the synthesis of cyclic nitramine derivatives similar to 1 was 4,5-dichloro-1,3-dioxolan-2-one (6, Scheme I). This compound, upon reacting with dinitramines, could lead to bicyclic carbonate esters. Initial experiments were conducted with the readily available ethylenedinitramine (EDNA), which, as its sodium salt in DMF, reacted with 6 to give the bicyclic carbonate ester (7). Treatment of this compound with boron tribromide led to ester cleavage and formation of the dibromide (8), the same product obtained from similar ester cleavage of 2,3-diacetoxy-1,4-dinitropyrazine². As reported previously³, we were unsuccessful in converting 8 into bicyclic nitramines by reaction with salts of EDNA or MEDINA because these nucleophiles, and others, readily debrominated 8 into the moderately stable olefin (9). Compound 9 was the first example of an alpha unsaturated nitramine.

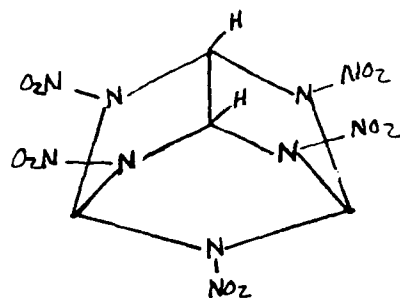
Similar to the above reactions, the triethylammonium salt of MEDINA reacted with (6, Scheme I) to yield the bicyclic carbonate ester (10). X-ray crystallographic analysis (R. Gilardi, NRL) confirmed the structure and showed a crystal density of 1.952. Although 10 was formed only in very low yield (7.5%), it was much easier to isolate and purify than the diacetoxy-dinitropyrazine (1). Sufficient quantities of 10 were prepared for further experimentation. Boron tribromide ester cleavage of 10 proceeded smoothly and in high yield to give the dibromide (2) as an oil, whose structure was established by NMR and mass spectrometry. Attempts were then made to convert 10 into bicyclo-HMX (11), or the analogous tetraazabicyclononane, by reaction with salts of MEDINA or EDNA, respectively. The triethylammonium salt of MEDINA reacted with 10, under various conditions, in acetonitrile, to give in all instances dark oils containing (by TLC) multiple components. No crystalline materials could be isolated from this mixture, whose NMR spectrum did not, in any case, show characteristic signal peaks predicted for bicyclo-HMX. Further reactions on 10 were conducted with the triethylammonium, sodium, and silver salts of EDNA in various solvents. Again, only multiple-component decomposition residues were obtained, from which no crystalline materials could be isolated.

An attempt was then made to debrominate 2 to the cyclic olefin (12) under mild conditions by means of triethyl phosphite, as was done with dibromide (8) to give the olefin (9). Extensive decomposition of 2 occurred under these conditions giving no isolable products. These results indicate that 12, if it is transiently formed at all in this and the above reactions of 2, is much more unstable than 9, and spontaneously decomposes into the multiple-component oils observed above. In view of the side-reactions encountered with displacement reactions on the imidazolidine and pyrazine dibromides, work with these compounds was discontinued.

Scheme I. Bicyclicnitramine Carbonates and Derivatives

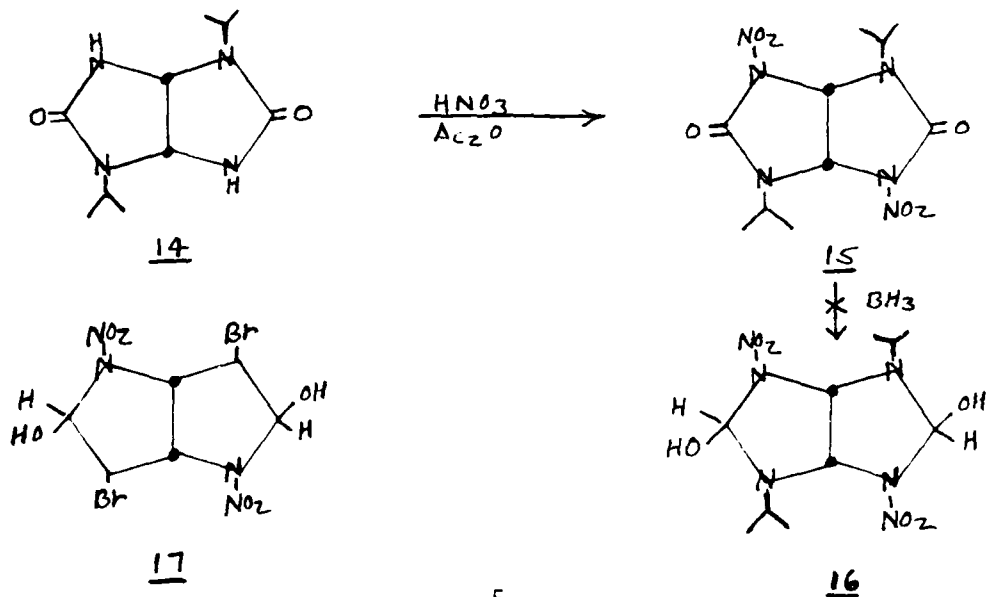


Tetraazabicyclooctanes which are substituted at the 3- and 7-positions can be useful intermediates for the synthesis of energetic polycyclic structures such as 13. Functionality at these positions might allow the *cis*-fused five-membered rings to be tied together to form the cage. Consequently,



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we are involved in the synthesis of tetraazabicyclooctanes in which functional groups such as hydroxyl, halogen, halomethyl, or amino can be introduced at the 3- and 7-positions. The condensation of substituted methylenebisamides with glyoxal is one synthetic approach which could be used, and work has begun on this method. Another approach would be to convert a substituted glycouril into a derivative suitable for cyclization into a caged structure. Diisopropyl glycouril (14) was chosen as the starting material for this approach because of its greater solubility properties in organic solvents, as compared to glycouril itself. Nitration of 14 with nitric acid-acetic anhydride gave the dinitro product (15). Attempts were then made to reduce the carbonyl groups of 15 to hydroxyl groups to give 16, with borane, under various conditions. Precedent for this reaction was the successful synthesis of the diol (17) from the corresponding carbonyl compound in the diaza-bicyclooctane series⁴. However, 15 was resistant to reduction with borane under mild conditions, and gave only decomposition products under more forcing conditions.



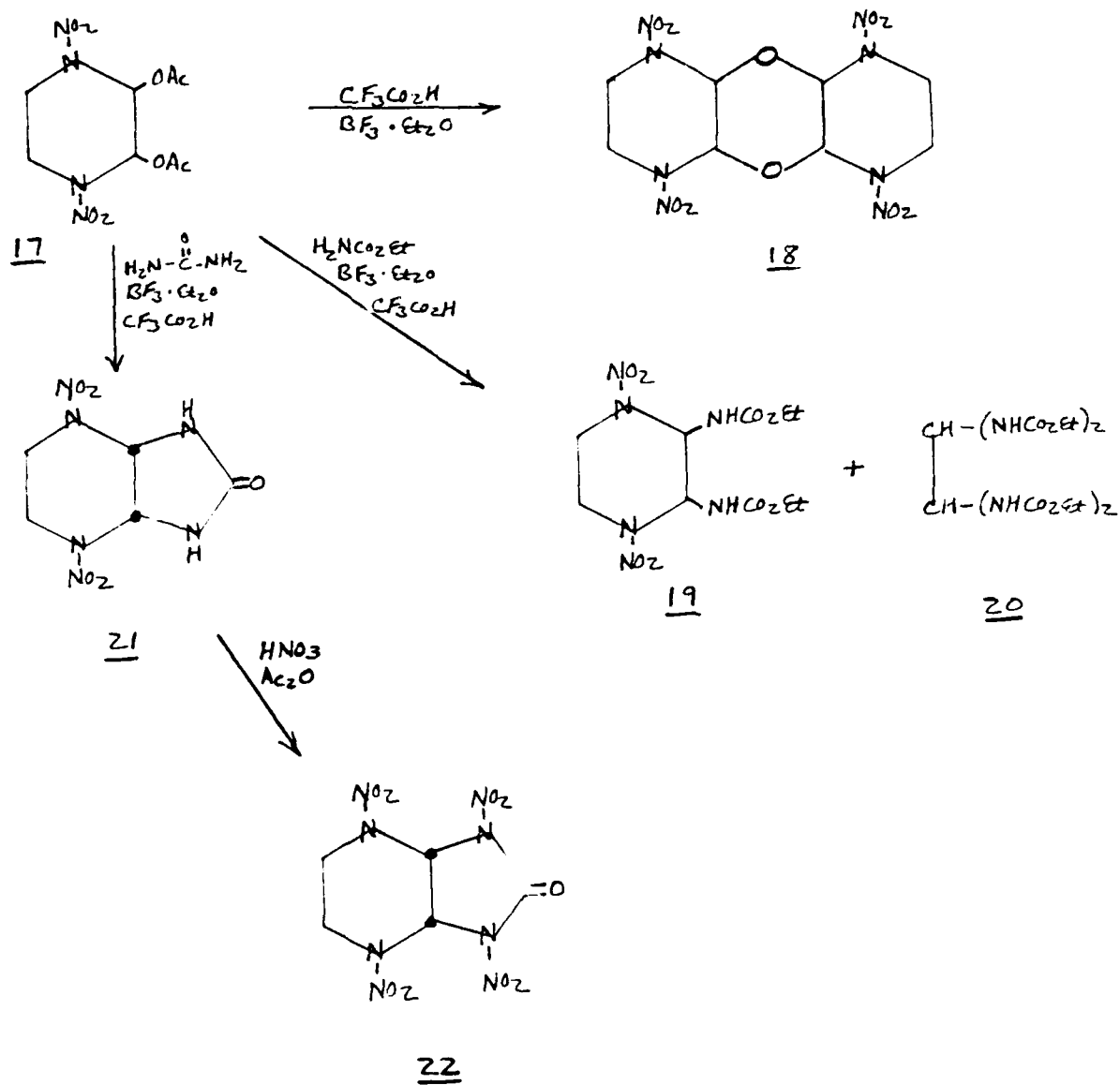
(b) Tetraazabicyclononanes

Several years ago we reported the synthesis of 2,3-diacetoxy-1,4-dinitropyrazine (17, Scheme II) by the reaction of EDNA with glyoxal in the presence of acetic anhydride². Further chemical transformations of 17 into 2,3-dihalides were described in a later report³. Unsuccessful attempts were made to convert 17 into a tetranitro-tetraazabicyclononane by reaction with MEDINA in trifluoroacetic acid under boron trifluoride catalysis. The major product, isolated in high yield, was the tricyclic ether (18). In fact, compound 18 was the only product isolated when MEDINA was present in large excess, or not present at all. The strongly acidic conditions in these reactions imply that 18 is formed by S_N1 type mechanisms, and that MEDINA is too acidic, itself, to react with incipient cations adjacent to the nitramine groups on the pyrazine. We anticipated that a more basic nitrogen species, such as an amide, used in excess, might intercept these cations, thus suppressing the formation of 18, and lead to the introduction of nitrogen functionality on the pyrazine ring.

Under the same reaction conditions mentioned above, but employing a four-fold excess of urethane instead of MEDINA, the diacetoxypyrazine (17) reacted to give a good yield of the bisurethane derivative (19). A by-product of this reaction was tetra(carbethoxyamino)ethane (20). Similarly, the reaction of 17 with an excess of urea gave the bicyclic urea (21), although in this case the yield was only about 20%. Nitration of 21 proceeded smoothly in nitric acid-acetic anhydride to give the tetranitro-tetraazabicyclononane (22) in almost quantitative yield. X-ray crystallographic analysis (R. Gilardi, NRL) confirmed the structure of 22 and showed a crystal density of 1.969 g/cc. This compound has been previously synthesized at Lawrence Livermore National Laboratory⁵.

These reactions, in which nitrogen is introduced onto a carbon bearing another nitrogen, to form an amination-type linkage, may be useful in the synthesis of more complex polycyclic systems. For instance, 2,3,5,6-tetraacetoxy pyrazines containing N-nitro, N-formyl and N-methylsulfonyl substituents are readily available,^{6,7} and could serve as starting materials for the synthesis of energetic tricyclic polynitramines.

Scheme II. Chemical Transformations of 2,3-Diacetoxy-1,4-Dinitropyrazine



EXPERIMENTAL SECTION

Melting points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained on a Varian EM-390 spectrophotometer. Chemical shifts are in ppm relative to TMS as internal standard. Mass spectral data were obtained on a Finnegan Model 4000 instrument (CI, CH_4). X-ray crystallographic analyses were performed by R. Gilardi at the Naval Research Laboratory, Washington, D. C.

1,1,2,2-Tetraacetoxyethane (3). - A solution of glyoxal trimeric dihydrate (21.0g, 0.1 mol) in acetic anhydride (200 mL) was refluxed for 20h, then treated with activated charcoal while still hot, and filtered. The filtrate was cooled in a refrigerator for 2 days and filtered to give white crystals (25.4g, 32.3%): mp 101-104°C. Recrystallization from ethanol gave white prisms: mp 102-104°C. Reported⁸ mp, 106-107°C.

1,2-Diacetoxy-1,2-dibromoethane (4). - A solution of boron tribromide in CH_2Cl_2 (100 mL of 1.0 M, 0.1 mol) was slowly added, over 30 min, to a stirred solution of tetraacetoxyethane (13.11g, 0.05 mol) in CH_2Cl_2 (50 mL) cooled in ice. The mixture was stirred for 30 min with the ice-bath removed, then refluxed for 1h, washed with water (3x50 mL), dried (MgSO_4) and evaporated to leave a tan solid residue. Recrystallization from hexane (charcoal) gave white crystals (1.02g, 6.7%): mp 83-84°C; ^1H NMR (CDCl_3) δ 6.96 (s, 2, CH), 2.27 (s, 6, CH_3 s). Anal. Calcd for $\text{C}_6\text{H}_8\text{Br}_2\text{O}_4$: C, 23.71; H, 2.65; Br, 52.58. Found: C, 23.88; H, 2.76; Br, 52.44.

Reaction of MEDINA with tetraacetoxyethane. - A solution of methylenedinitramine (1.36g, 10 mmol), tetraacetoxyethane (2.62g, 10 mmol), and boron trifluoride etherate (2.84g, 20 mmol) in acetic acid (20 mL) was stirred at room temperature for 3 days. The solvent was evaporated under reduced pressure and the pale yellow residue was dissolved in CH_2Cl_2 (50 mL) and washed with water, 5% aqueous sodium bicarbonate, dried (MgSO_4) and evaporated to leave a colorless residue. The residue was dissolved in benzene (5 mL) and placed on a column of silica gel (50g, EM grade 62). The first 350 mL of eluent (benzene) contained no material. The next 250 mL (10% CH_3CN -benzene) contained about 500 mg of tetraacetoxyethane. The final 200 mL (20% CH_3CN -benzene) yielded 300 mg (10.7%) of a white solid, mp 101-102°C (ethanol). This was shown, by X-ray crystallographic analysis, to be 1,5-diacetoxy-2,4-dinitro-2,4-diazapentane (5): ^1H NMR (CDCl_3) δ 5.98 (s, 4, CH_2Os), 5.92 (s, 2, CH_2), 2.17 (s, 6, CH_3 s). Anal. Calcd for $\text{C}_7\text{H}_{12}\text{N}_4\text{O}_8$: C, 30.00; H, 4.32; N, 20.00. Found: C, 29.92; H, 4.22; N, 19.57.

2,5-Dinitro-2,5-diaza-7,9-dioxabicyclo[4:3:0]nonan-8-one (7). - Aqueous sodium hydroxide (20 mL of 10N, 0.2 mol) was added dropwise, over 15 min, to a stirred solution of ethylenedinitramine (15.0g, 0.1 mol) in DMF (250 mL), cooled in a cold water bath. A white solid precipitated from the solution. The mixture was stirred for 20 min, and then a solution of 4,5-dichloro-1,3-dioxolan-2-one (22.2g, 0.12 mol, of 85% technical grade - Aldrich Chem. Co.) in DMF (50 mL) was added dropwise over 15 min. After stirring for 4h at room temperature, the DMF was removed under reduced pressure and the residue extracted with ethyl acetate (150 mL). The organic extract was washed with 5% aqueous sodium bicarbonate (2x50 mL), saturated aqueous salt, dried (MgSO_4) and evaporated to leave 11.2g of a white solid mixture of products, including some ethylenedinitramine. Recrystallization from CH_3CN -isopropyl ether

afforded **7** as white crystals (5.3g, 22.6%): mp 186-187°C; ^1H NMR δ 7.52 (s, 2, CHs), 4.77 and 4.27 (m, 4, CH_2 s); mass spectrum m/z (relative intensity) 275 (2, $M+41$), 263 (5, $M+29$), 235 (43, $M+1$), 191 (45), 144 (29), 99 (100). Anal. Calcd for $\text{C}_5\text{H}_6\text{N}_4\text{O}_7$: C, 25.65; H, 2.58; N, 23.93. Found: C, 25.66; H, 2.55; N, 24.05.

trans-2,3-Dibromo-1,4-dinitropyrazine (8).- Boron tribromide (2.0 mL of 1.0 M in CH_2Cl_2 , 2.0 mmol) was added to a suspension of the cyclic carbonate (**1**, 234 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) and the mixture stirred at room temperature for 90 min. The solution was diluted with CH_2Cl_2 (30 mL) and washed with water, 5% aqueous sodium bicarbonate, dried (MgSO_4) and evaporated to leave a solid residue which was triturated with hexane and filtered to give white crystals (260 mg, 78%), mp 131-132°C. This product was identical (mp, NMR) to the product obtained by ester cleavage of 2,3-diacetoxy-1,4-dinitropyrazine³.

5,7-Dinitro-5,7-diaza-1,3-dioxabicyclo[3:3:0] octan-2-one (10).- A solution of triethylamine (10.1g, 0.1 mol) in CH_3CN (25 mL) was added dropwise to a stirred solution of methylenedinitramine (6.8g, 0.05 mol) and 4,5-dichloro-1,3-dioxolan-2-one (9.60g, 0.052 mol, of 85% technical grade-Aldrich Chem. Co.) in CH_3CN (150 mL), cooled in ice, over 20 min. Stirring was continued at 0°C for 15 min and then for 2h longer with the bath removed. The mixture was filtered to remove 13.0g (13.78-theor.) of triethylamine·HCl and the filtrate was evaporated to leave a yellow residue of oil and solid. This mixture was dissolved in the minimum amount of warm CH_3CN and placed on a column of silica gel (40g, EM grade 62). Elution was conducted with 10% CH_3CN -benzene until no more organic material appeared in the eluted fractions. The combined fractions were evaporated and the residue was triturated with ethanol and filtered to yield a white solid (830mg, 7.5%), mp 198-203°C (dec.). Recrystallization from CH_3CN -isopropyl ether gave colorless prisms: mp 210-211°C (dec.); ^1H NMR (Acetone- d_6) δ 7.13 (s, 2, CHs), 6.00 (q, 2, CH_2); mass spectrum, m/z (relative intensity) 261 (0.5, $M+41$), 249 (1, $M+29$), 221 (7, $M+1$), 177 (8), 159 (8), 114 (100). Anal. Calcd for $\text{C}_4\text{H}_4\text{N}_4\text{O}_7$: C, 21.83; H, 1.83; N, 25.46. Found: C, 21.97; H, 1.88; N, 25.26. X-ray crystallographic analysis confirmed the structure and showed a crystal density of 1.952.

4,5-Dibromo-1,3-dinitroimidazolidine (2).- Boron tribromide (10 mL of 1.0 M in CH_2Cl_2 , 10 mmol) was added, over 3 min, to a stirred suspension of the cyclic carbonate ester (**10**, 1.10g, 5 mmol) in CH_2Cl_2 (100 mL), cooled in ice. Stirring was continued for 3h with the ice bath removed. The solution was then washed with water (2x50 mL), 5% aqueous sodium bicarbonate (2x70 mL), dried (MgSO_4) and evaporated under reduced pressure. The residue was redissolved in benzene (10 mL) and evaporated, and this operation was repeated again to leave a pale yellow oil (1.58g, 98.7%). ^1H NMR (CD_2Cl_2) δ 6.71 (s, 2, CHs), 5.70 (s, 2, CH_2); mass spectrum, m/z (relative intensity) 323 (2, $M+1$, Br = 81), 321 (3), 319 (2), 241 (4, $M+1$ -HBr, Br = 81), 239 (4), 114 (100), 69 (99).

2,6-Diisopropyl-4,8-dinitrobicyclo[3:3:0]octa 3,7-dione (15).- Acetic anhydride (20 mL) was added dropwise, with stirring, to 100% nitric acid (20 mL), cooled in a salt-ice bath, at such a rate that the temperature stayed below 5°C. After stirring for 15 min, 1,4-diisopropylglycouril⁹ (4.5g, 0.02 mol) was added in portions over 15 min, and the solution maintained at salt-ice temperature for 1h, and then poured onto ice (200 mL). The

precipitate was filtered and dried to yield a white solid (5.67g, 90%): mp 209-210°C (dec). ^1H NMR ($\text{Me}_2\text{CO}-d_6$) δ 6.72 (s, 2, CHs-ring juncture), 4.27 (septet, 2, CHNs, $J = 8$ Hz), 1.40 (t, 12, CH_3 s, $J = 8$ Hz).

Attempted reduction of (15). - A solution of 15 (316mg, 1.0 mmol) and borane (4.5 mL of 1.0M in THF, 4.5 mmol) in THF (10 mL) was refluxed for 1h. The solution was then concentrated to 5 mL and water (15 mL) was added. This mixture was concentrated to about 10 mL on a water pump, then cooled and filtered to yield a white solid (270 mg), mp 190-195°C (dec). This was identified as starting material, by NMR. When the reduction was carried out in dioxan, for 20h at reflux, starting material was again recovered, along with minor amounts of unidentified decomposition products.

2,3-Bis-(carbethoxyamino)-1,4-dinitropyrazine (19). - A solution of 17 (14.61g, 0.05 mol), urethane (35.6g, 0.4 mol), and boron trifluoride etherate (14.19g, 0.1 mol) in trifluoroacetic acid (125 mL) was stirred at room temperature for 5h. The solvent was evaporated at reduced pressure and the residue diluted with water (200 mL), cooled in an ice-bath, and filtered to give a white solid (14.8g). This solid was extracted with hot ethyl acetate (200 mL) and filtered to remove an insoluble white material (3.1g), which was identified as 1,1,2,2-tetra(carbethoxyamino)ethane (20), by IR and NMR spectroscopy¹⁰. The filtrate was evaporated under vacuum and the residue triturated with isopropyl ether and filtered to yield 19 as a white solid (10.6g, 60.5%), mp 198-200°C. Recrystallization from ethyl acetate-isopropyl ether gave colorless crystals: mp 200-201°C; ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 8.69 (d, 2, NHs), 6.46 (d, 2, CHs), 4.42 and 4.09 (m, 4, CH_2 Ns), 4.26 (q, 4, CH_2 Os), 1.24 (t, 6, CH_3 s). Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{N}_4\text{O}_8$: C, 34.28; H, 5.18; N, 23.99. Found: C, 34.41; H, 5.12; N, 23.88.

1,4-Dinitro-1,4,6,8-tetraazabicyclo[4:3:0]nonan-7-one (21). - A solution of 17 (1.46g, 5.0 mmol), urea (2.40g, 40 mmol), and boron trifluoride etherate (1.42g, 10 mmol) in trifluoroacetic acid (20 mL) was stirred at 55°C for 4h, and then at room temperature overnight (17h). The solvent was evaporated at reduced pressure and the residue diluted with water (25 mL), cooled in an ice-bath, and filtered to give a cream-colored solid (225mg, 19.4%), mp 220°C (rapid dec). Recrystallization from CH_3CN gave colorless plates: mp 225°C (rapid dec); ^1H NMR ($\text{Me}_2\text{SO}-d_6$) δ 7.99 (s, 2, NHs), 6.60 (s, 2, CHs), 4.52 and 3.92 (m, 4, CH_2 s). Anal. Calcd for $\text{C}_5\text{H}_8\text{N}_6\text{O}_5$: C, 25.87; H, 3.47; N, 36.20. Found: C, 25.95; H, 3.76; N, 35.93.

1,4,6,8-Tetranitro-1,4,6,8-tetraazabicyclo[4:3:0]nonan-7-one (22). - Absolute (100%) nitric acid (1.0 mL) was added dropwise, over 2 min, with stirring, to acetic anhydride (1.0 mL), cooled in ice. After stirring at 0°C for 20 min, 21 (232mg, 1.0 mmol) was added all at once. The solid dissolved, and after about 5 min, a white precipitate appeared. Stirring was continued at 0°C for 30 min and then at room temperature for 4h. The mixture was again cooled in ice, CH_2Cl_2 (5 mL) was added, and then filtered to yield 22 as a white solid (321mg, 99.7%), mp 188°C (rapid dec). Recrystallization from ethyl acetate-isopropyl ether gave colorless prisms, mp 202°C (rapid dec). X-ray crystallographic analysis confirmed the structure and showed a crystal density of 1.969. ^1H NMR ($\text{Me}_2\text{CO}-d_6$) δ 8.12 (s, 2, CHs), 4.87 and 4.29 (m, 4, CH_2 s). Anal. Calcd for $\text{C}_5\text{H}_6\text{N}_8\text{O}_9$: C, 18.64; H, 1.88; N, 34.78. Found: C, 18.96; H, 2.08; N, 34.46.

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